

PATENT APPLICATION

OF

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FOR

**POLYMERIC COMPOSITIONS
USEFUL IN PLASTIC RESINS**

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POLYMERIC COMPOSITIONS USEFUL IN PLASTIC RESINS

The present invention relates to polymeric compositions. These compositions are useful in improving the properties and processability of plastic resins. The present invention also pertains to processes for preparing such polymeric compositions, as well as processes for preparing plastic matrixes containing the same.

It has been known for many decades that plastic resins often do not possess the physical or processing characteristics necessary to make them commercially viable. Accordingly, polymeric compositions are often added to enhance the plastics' characteristics.

One type of common plastic additive is an impact modifier. Impact modifiers are used for endowing various plastic resins with impact resistance. Many commercial impact modifiers are core/shell type graft copolymer particles prepared by graft-polymerizing a vinyl monomer (forming the shell layer) to crosslinked particles containing a rubber component (forming the core portion). It is presumed that the rubber component in the core portion endows the impact modifying effect and the vinyl component in the shell layer endows compatibility (namely, dispersibility) to matrix resin.

There is known, for example, an impact modifier which is prepared by graft-polymerizing a vinyl monomer to a polybutadiene rubber having a low glass transition temperature (hereinafter "Tg"). As used herein, the term "low Tg" refers to a glass transition temperature not greater than 20°C. Impact modifiers prepared by graft-polymerizing a vinyl monomer into an acrylic rubber having a low Tg are also known.

However, the plastic additives industry is continually seeking to improve the performance of their additives. For example, an impact modifier's impact resistance properties have been inversely proportional to their thermal stability and weatherability properties. Specifically, polybutadiene rubber-containing impact modifiers often have better impact resistance and poorer thermal stability and weather resistance when compared to their acrylic rubber-containing counterpart. On the other hand, acrylic rubber-containing impact modifiers often have better thermal stability and weather resistance and poorer impact resistance when compared to their polybutadiene rubber-containing counterpart.

There have been a number of attempts to improve the physical, processing and performance properties of plastic additives, especially impact modifiers. Some examples of such attempts are set out below.

US Patent 6,011,116 discloses impact modifier particles having a rubber portion made from an isobutylene polymer and a vinyl polymer. According to that patent, molecular chains of the isobutylene polymer and the vinyl polymer are intertwined with each other so that the polymers cannot be separated substantially from each other.

US Patent 6,201,064 discloses impact modifier particles made from graft copolymer particles prepared by graft-copolymerizing at least one vinyl monomer onto crosslinked rubber particles comprising an isobutylene polymer component and an organosiloxane polymer component.

US Patent 6,306,961 discloses a thermoplastic resin composition which includes a thermoplastic resin component and an impact modifier component. The impact modifier component includes impact modifier particles which have a void filled rubber core. According to that patent, the volumetric proportion of the voids in the rubber core portion of the impact modifier particles ranges from 1 to 70% by volume.

While the above patents solve some of the problems facing impact modifiers, they do so at the expense of creating others. Accordingly, the plastic additives industry and the plastic manufacturing industry continues to seek out new and better plastic additives.

Therefore, one object of the present invention is to provide a novel polymeric composition which provides excellent impact resistance, weather resistance and thermal stability when added to a plastic resin system.

Another object of the present invention is to provide a novel plastic resin system which has excellent impact resistance, weather resistance and thermal stability.

These and other objects will be apparent to those skilled in the art after reading the specification and appended claims.

The novel polymeric compositions of the present invention include at least one population of polymeric particles having a rubber-containing portion which includes at least one of the following blends: (a) an organosiloxane polymer component and an isobutylene polymer component; (b) a vinyl polymer component and an isobutylene polymer component;

or (c) an organosiloxane polymer component, a vinyl polymer component and an optional isobutylene polymer component.

In one embodiment, the isobutylene polymer component of the rubber-containing portions comprising blend (a), (b) or (c) is present in an amount of at least 1 weight percent of the polymeric particle. In this embodiment, at least one of the following conditions must also exist:

1. At least a portion of the polymeric particles must have a void-containing rubber portion, wherein the volumetric proportion of the voids defined in the rubber portion ranges from 1 to 90%.
2. The polymeric composition must further include at least 1 weight percent of a processing oil component.
3. The polymeric composition must further include at least 2 weight percent of a processing aid component.
4. The polymeric composition must contain at least two different populations of polymeric particles, wherein each has a rubber-containing portion, and wherein the difference is in at least one of the following: the void concentration in the rubber-containing portions of each population, the chemical composition of each population, the average particle size of each population, or the shape of each population.

In another embodiment, the isobutylene polymer component of rubber-containing portions comprising blend (a), (b) or (c) is present in an amount less than 1 weight percent of the polymeric particles. In this embodiment, the features 1, 2, 3, or 4 set out in the prior paragraph do not need to be present. However, it is within the scope of this embodiment of the invention for any one or more of those features to be present when practicing this embodiment.

The novel plastic resin systems comprising yet another embodiment of the invention include a plastic resin component and an impact modifier component. The impact modifier component comprises at least one of the novel polymeric compositions set out above.

The term “units derived from” used herein refers to polymer molecules that are synthesized according to known polymerization techniques wherein a polymer contains “units derived from” its constituent monomers.

The term “molecular weight” used herein refers to the weight average molecular weight of polymer molecules as determined by the gel permeation chromatography method.

The term “alkyl (meth)acrylate” used herein refers to both alkyl acrylate and alkyl methacrylate monomer compounds.

The term “stage” used herein is intended to encompass its broadest possible meaning, including the meaning conveyed in prior art such as in U.S. Patent 3,793,402 which offers various means for achieving “staged” polymers.

The term “parts” used herein is intended to mean “parts by weight”. Unless otherwise stated, “total parts by weight” do not necessarily add to 100.

The term “weight percent” used herein is intended to mean “parts per hundred by weight” wherein the total parts add to 100.

The term “particle size” used herein refers to the mean particle diameter of a population of particles.

The novel polymeric compositions of the present invention include polymeric particles having a rubber-containing portion which includes at least one of the following: (a) an organosiloxane polymer component; (b) a vinyl polymer component; or (c) an organosiloxane polymer component and a vinyl polymer component. In (a) and (b), the rubber-containing core portion further includes an isobutylene polymer component. In (c), an isobutylene polymer component is optional.

The compositional make up of the polymeric particles of this embodiment depends, in part, upon the concentration of the isobutylene polymer component in the rubber-containing portion. Specifically, if the isobutylene polymer component is present in an amount of at least 1 weight percent, at least one of the following four conditions must also exist:

1. At least a portion of the polymeric particles must have a void-containing rubber portion, wherein the volumetric proportion of the voids defined in the rubber portion ranges from 1 to 90%.

2. The polymeric composition must further include at least 1 weight percent of a processing oil component.

3. The polymeric composition must further include at least 2 weight percent of a processing aid component.

4. The polymeric composition must contain at least two different populations of polymeric particles, wherein each has a rubber-containing portion, and wherein the difference is in at least one of the following: the void concentration in the rubber-containing portions of each population, the chemical composition of each population, the average particle size of each population, or the shape of each population.

Each of these will now be discussed in detail.

Presence Of A Void-Containing Rubber Portion

Firstly, the polymeric composition includes at least one population of polymeric particles which have a void-containing rubber portion in which the volumetric proportion of the voids defined within the rubber portion ranges from 1 to 90%.

The void-containing rubber particles can be prepared by applying techniques used in the field of paints. For example, there are (a) methods of preparing a W/O/W emulsion and polymerizing a monomer of the O layer (O: hydrophobic, W: hydrophilic); (b) methods of hollowing by swelling core-shell particles having a swellable core at a temperature of not less than T_g of the shell layer; (c) methods of two stage polymerization of polymers having different solubility parameters; (d) methods of finely dispersing a polymerizable monomer mixture containing a crosslinkable monomer and hydrophilic monomer and an oily substance in water to give a O/W emulsion and then polymerizing for crosslinking and removing the oily substance after the crosslinking; and (e) methods of using a phenomenon, in which a carboxylic acid unit copolymerized in the particle moves in the particle under acidic or alkaline conditions as set out in "*Application of Synthetic Latex*" by Takaaki Sugimura, *et al*, pp. 285, published by Kobunshi Kankokai (1993).

In this specific embodiment, the void-containing rubber particles can be prepared by any of the method known to those skilled in the art, including the methods set out in the prior paragraph. However, for illustrative purposes, one method of practicing process (b) is described below.

First, rubber polymer particles or hard polymer particles are used as a core. To an aqueous dispersion or latex of these polymer particles are added a monomer mixture for a rubber polymer forming a shell and an oily substance for swelling the polymer particles of the core. Thus, the polymer particles of the core are swelled by the oily substance. At the time when the polymer particles are swelled enough, the monomer mixture is polymerized to form the shell comprising the rubber polymer. Then, by removing the oily substance swelling the core, the core is shrunk and a cavity arises between the shell of rubber polymer and the polymer particle of the core. Thus, the void-containing rubber particles can be obtained.

Accordingly, the polymer particles to be used as a core for method (b) are, preferably, those which can be swelled by an oily substance. Examples of materials that can be used for this purpose include: a diene rubber such as a butadiene rubber, styrene-butadiene rubber or acrylonitrile-butadiene rubber, an acrylic rubber such as a butyl acrylate rubber, butadiene-butyl acrylate rubber, 2-ethylhexyl acrylate-butyl acrylate rubber, 2-ethylhexyl methacrylate-butyl acrylate rubber, stearyl acrylate-butyl acrylate rubber, dimethylsiloxane-butyl acrylate rubber, a composite rubber of a silicone rubber and butyl acrylate rubber or butyl methacrylate rubber, a silicone rubber such as a polydimethylsiloxane rubber, an olefin rubber such as an ethylene-propylene rubber or ethylene-propylene-diene rubber; and a hard polymer such as polystyrene, styrene-acrylonitrile copolymer, and styrene-methyl methacrylate copolymer. From the viewpoint of improving impact resistance, the rubber polymers are typically preferable.

The void-containing rubber particles have at least one cavity (hollow part) defined therein. The number of the cavities is not limited to one. The shape of the cavity or cavities is also not limited; and, the cavity or cavities may be in the form of sphere, flat sphere, pore or honeycomb. Also, on the inner surface of the cavity or cavities, there may exist concave or convex or protrusions.

The volumetric proportion (cavity ratio) of the cavity to the rubber particle typically ranges from 1 to 90%. It is within the scope of this invention for cavity ratio to range from 5 to 80%; or from 10 to 70%, or from 15 to 60%. The preferred cavity ratio depends, in part, on the desired properties of the resulting polymeric composition. After reading this specification, those skilled in the art will be able to determine the cavity ratio which meets their needs.

The average particle size of the void-containing rubber particles typically ranges from 50 to 2,000 nm. It is within the scope of this invention for these void-containing rubber particles to have an average particle size ranging from 75 to 1,750 nm; or from 100 to 1,500 nm, or from 200 to 1,000 nm. The preferred average particle size of the void-containing rubber particles depends, in part, on the desired properties of the resulting polymeric composition. After reading this specification, those skilled in the art will be able to determine the average particle size which best suits their needs.

The rubber component of these void-containing rubber particles typically has a Tg of not greater than 20°C. It is, however, within the scope of this invention for the Tg of this rubber component to be less than 0°C ; or less than -20°C , or less than -40°C . The preferred Tg of the rubber component depends, in part, on the desired properties of the resulting polymeric composition. After reading this specification, those skilled in the art will be able to determine Tg which best suits their needs.

In this embodiment, a crosslinking agent can, optionally be present in the void-containing rubber portion of the polymeric particles. If present, the concentration of the crosslinking agent typically ranges from 0.01 to 5 weight percent. It is within the scope of this invention for the concentration of the crosslinking agent to range from 0.05 to 4 weight percent; or from 0.1 to 3 weight percent; or from 0.15 to 2 weight percent; or from 0.2 to 1 weight percent. The above weight percentages are based on the total weight of the void-containing rubber portion.

Examples of crosslinking agents that can be used when practicing this invention include: allyl methacrylate, divinylbenzene, diallyl phthalate, polyethylene glycol dimethacrylate, 1,3-butylene glycol dimethacrylate, and ethylene glycol dimethacrylate. These may be used solely or in a combination use of two or more thereof.

Presence of a Processing Oil Component

Secondly, the polymeric composition further includes at least 1 weight percent of a processing oil component. In this embodiment, the percentage of the weight of the processing oil component to the weight of the total population of polymeric particles typically ranges from 1 to 30 weight percent; or from 2 to 25 weight percent; or from 3 to 20 weight percent.

Moreover, the ratio of the weight of the processing oil component to the weight of the polymeric component typically ranges from 0.1:10 to 5.0:10. It is within the scope of this embodiment of the invention for this weight ratio to range from 0.5:10 to 4.5:10; or from 1.0:10 to 4.0:10; or from 1.5:10 to 3.5:10. The actual ratio used will depend upon the relative solubility of the processing oil component in the particular plastic resin and the polymeric composition. However, when the ratio is too large, problems of over lubrication can be encountered.

The term “processing oil” as it relates to the term “processing oil component” includes: (a) polymers which have a weight average molecular weight (Mw) of less than 5,000 g/mol; (b) alkylacrylates having an alkyl group containing 12 or more carbon atoms; (c) esters containing carboxylic acids or alcohols with 12 or more carbon atoms; (d) vegetable oils; (e) marine oils; (f) industrial oils; (g) palm oils; (h) animal fats; and (i) mineral oils. Examples of (a) include: polybutene, polydimethylsiloxane, polypropylene, polybutadiene, and polyisoprene. Examples of (b) include: stearyl (meth)acrylate, and lauryl (meth)acrylate. Examples of (c) include: methyl stearate, ethyl stearate, butyl stearate, and stearyl citrate. Examples of (d) include: sunflower oil, peanut oil and olive oil. An example of (e) includes: cod liver oil. Examples of (f) include: castor oil and linseed oil. An example of (g) includes: coconut oil. An example of (h) includes: tallow. Examples of (i) include: paraffinic oils with saturated straight or branched chains or rings containing at least 20 carbon atoms; naphthenic or relatively naphthenic, that is, containing saturated monocyclic (from 4 to 12 carbon atoms) or polycyclic (from 13 to 26 carbon atoms) hydrocarbon oils; microcrystalline wax, paraffin wax and low molecular weight polyolefins such as polyethylene wax, either in liquid, powder or flake form; aromatic oils with a minimum molecular weight of 300 g/mol; and white mineral oils which are a complex mixture of saturated paraffinic and naphthenic hydrocarbons and are free of aromatic compounds, sulphur containing compounds, acids and other impurities.

Under certain preferred circumstances, the processing oil component comprises mineral oils. If employed, the preferred mineral oils are typically those which are easy to handle and do not present environmental or health concerns. Such include those which have a low viscosity and those with a low volatility at the temperatures used during the milling and extrusion blending processes. Examples of specific mineral oils which have these properties include heavy mineral oils such as those termed USP mineral oils (they typically have a density ranging of from 0.86 - 0.90 g/ml), and light mineral oils (they typically have a density

ranging of from 0.80-0.85g/ml). One preferred heavy mineral has a density of 0.86 g/ml; and one preferred light mineral oil has a density of 0.84 g/ml, both of these oils are available from the Aldrich Chemical Company.

When practicing this specific embodiment, it is contemplated that the processing oil component can be mixed with at least a portion of the population of polymeric particles by at least one of the following methods: (a) combining the processing oil directly or indirectly with the polymeric particles after the polymeric particles have been formed, or (b) adding the processing oil at the start of, or at some point during, the reaction process used to prepare the polymeric particles.

One example of a preferred process for combining at least one processing oil with the polymeric particles includes the following steps: (a) mixing together an aqueous surfactant solution, a first monomer material and an initiator; (b) heating the resulting mixture to polymerize the monomers; optionally (c) combining the resulting polymerized product from step (b) with a second monomer, a further initiator and further surfactant and heating the resulting mixture to produce a core/shell latex; and (d) isolating the resultant core/shell polymeric particles; wherein the processing oil is added to the reaction mixture during any one or more of the steps (a), (b), (c) or (d). It also within the scope of this embodiment for either at least a portion of the processing oil to be added after step (d), or for all of the processing oil to be added after step (d).

Presence of a Processing Aid Component

Thirdly, the impact modifier composition further includes at least 1 weight percent of a processing aid component. In this embodiment, the percentage of the weight of the processing aid component to the weight of the total population of polymeric particles typically ranges from 1 to 30 weight percent; or from 2 to 25 weight percent; or from 3 to 20 weight percent.

In accordance with this embodiment, the processing aid component comprises at least one population of processing aid particles. The population of processing aid particles can include single-stage particles, two-stage particles, or multi-stage polymer particles, as well as core/shell polymer particles.

When practicing this embodiment, the processing aid particles are typically comprised of polymerized units derived from one or more ethylenically unsaturated monomers.

Typically, such monomers include at least one of the following: vinyl aromatics, butadiene, alkyl (meth)acrylates, and (meth)acrylonitriles.

As used in this embodiment, the terms “alkyl (meth)acrylate” refers to a C₂ to C₁₂ alkyl (meth)acrylate. It is also within the scope of this invention for the term alkyl (meth)acrylate to refer to a C₂ to C₁₀ alkyl (meth)acrylate, or a C₂ to C₈ alkyl (meth)acrylate.

In certain preferred embodiments, the processing aid particles contain at least 50 weight methyl methacrylate copolymerized with up to 50 parts by weight of at least one of the following: alkyl (meth)acrylates, styrene, and (meth)acrylonitrile. It is within the scope of this embodiment of the invention for the processing aid particles to contain at least 75 weight methyl methacrylate copolymerized with up to 25 parts by weight of at least one of the following: alkyl (meth)acrylates, styrene, and (meth)acrylonitrile.

In this embodiment, the processing aid particles can include “hard” polymeric particles having a Tg of at least 25°C; or at least 35°C; or at least 45°C, or at least 55°C. It is, however, within the scope of this invention for the processing aid particles to include “soft” polymeric particles having a Tg of at most 20°C; or at most 0°C; or at most -20°C; or at most -40°C.

The molecular weight of the processing aid particles is typically greater than 100,000 g/mol. Generally, the molecular weight of the processing aid particles is greater than 1,000,000 g/mol. If the processing aid particles used in this embodiment include “soft” polymeric particles as defined above, then, additional advantageous results can be observed when their molecular weight is at least 2,000,000 g/mol.; or at least 3,000,000 g/mol., or at least 4,000,000 g/mol., or at least 5,000,000 g/mol.

The upper limit of the molecular weight for the hard or soft polymeric particles of the processing aid is determined, in part, by the processing conditions to which they are exposed, as well as their desired end use. Typically, their molecular weight is less than 12,000,000 g/mol., or less than 10,000,000 g/mol, or less than 8,000,000 g/mol.

Hard polymeric processing aid particles may be formed from homo- or copolymers of monomers such as styrene, methyl methacrylate, butyl acrylate, and ethyl acrylate, especially when the particle is prepared as a single-stage polymer particle. Although it is preferred that the processing aid particles contain no crosslinker, the polymers may contain one or more units derived from multifunctional monomers containing two or more double bonds, such as

from about 0.1 to about 5% of at least one of ALMA, allyl acrylate, DALMA, diallyl fumarate, divinylbenzene, a di- or triacrylate ester of a polyol, or a di- or trimethacrylate ester of a polyol.

Soft polymeric processing aid particles may comprise at least a first polymeric stage, wherein at least 50 weight percent of the first polymeric stage comprises a first polymeric component having units derived from one or more of the following: butadiene, and alkyl (meth)acrylates. Thus, the polymeric compositions which have a first polymeric stage comprising copolymers of butadiene and an alkyl (meth)acrylate(s), in any ratio, are encompassed by this invention.

The preferred first polymeric stage of such soft polymeric processing aid particles depends, in part, on the processing conditions to which the processing aid particles are exposed, as well as their desired end use. In one preferred embodiment, at least 50 weight percent of the first polymeric stage comprises a first polymeric component having units derived from one or more alkyl (meth)acrylate, or at least 60 weight percent of one or more alkyl (meth)acrylate, or at least 70 weight percent of one or more alkyl (meth)acrylate, or at least 80 weight percent of one or more alkyl (meth)acrylate.

The upper weight percent limit of the first polymeric component of soft polymeric processing aid particles also depends, in part, on the processing conditions to which the polymeric compositions are exposed, as well as their desired end use. In one preferred embodiment, 100 weight percent of the first polymeric stage comprises a first polymeric component having units derived from one or more alkyl (meth)acrylate, or at most 95 weight percent of one or more alkyl (meth)acrylate, or at most 90 weight percent of one or more alkyl (meth)acrylate, or at most 85 weight percent of one or more alkyl (meth)acrylate.

In the above illustrative examples wherein the first polymeric stage of the soft polymeric processing aid particles comprises a first polymeric component having units derived from one or more alkyl (meth)acrylate, in one preferred embodiment, the first polymeric component has units derived from at least one of the following: ethyl acrylate, butyl acrylate, hexyl acrylate, octyl acrylate, or 2-ethylhexyl acrylate. In another preferred embodiment, the first polymeric component of the soft processing aid particles has units derived from at least one of the following: ethyl acrylate, butyl acrylate, or 2-ethylhexyl acrylate. In still another preferred embodiment, the first polymeric component of the soft processing aid particles has units derived from ethyl acrylate.

In instances where the first polymeric component is less than 100 weight percent of the first polymeric stage, the remaining weight percentage can be made up of at least a second polymeric component. It is within the scope of this embodiment of the invention for there to be a plurality of subsequent polymeric components.

If present, the preferred amount of the second polymeric component depends, in part, on the processing conditions to which the polymeric compositions of the present invention are exposed, as well as their desired end use. In one preferred embodiment, at least 5 weight percent of the first polymeric stage comprises a second polymeric component, or at least 10 weight percent of the first polymeric stage comprises a second polymeric component, or at least 15 weight percent of the first polymeric stage comprises a second polymeric component.

The upper weight percent limit of the second polymeric component present also depends, in part, on the processing conditions to which the polymeric compositions of the present invention are exposed, as well as their desired end use. In one preferred embodiment, 50 weight percent of the first polymeric stage comprises a second polymeric component, or at most 40 weight percent of the first polymeric stage comprises a second polymeric component, or at most 30 weight percent of the first polymeric stage comprises a second polymeric component.

If present, the second polymeric component can be any suitable polymeric compound that yields a Tg of 20°C or less for the final polymeric composition. Examples of such suitable polymeric compounds include: other C₁ to C₁₈ alkyl (meth)acrylates, isoprene, vinyl acetate, styrene, alpha methyl styrene, acidic monomers such as acrylic acid or isobutylene, (meth)acrylonitrile, *etc.*

The preferred second polymeric component depends, in part, by the processing conditions to which the polymeric compositions of the present invention are exposed, as well as their desired end use. If used as a plastic additive, in one preferred embodiment, the second polymeric component comprises at least one of the following: C₁ to C₁₈ alkyl (meth)acrylates, alpha methyl styrene, styrene, acidic monomers such as (meth)acrylic acid. In another preferred embodiment, the second polymeric component comprises at least one of the following: C₁ to C₁₈ alkyl (meth)acrylates.

The first polymeric stage can also contain units derived from at least one multi-unsaturated monomer. If present, the concentration of such units ranges from 0.01 weight

percent to 5 weight percent of the total weight of the core portion. The multi-unsaturated monomer may be one in which the unsaturated groups are similar and of equal reactivity, such as in divinyl benzene, divinyl adipate, ethylene glycol dimethacrylate, butylene glycol diacrylate, trimethylolpropane trimethacrylate, and the like. On the other hand, the multi-unsaturated monomer may be one in which the unsaturated groups are dissimilar and of unequal reactivity, such as in diallyl maleate, allyl methacrylate, allyl acrylate, and the like.

The processing aid particles used when practicing this embodiment can be prepared by any means known to those skilled in the art. One example of a known process is emulsion polymerization (*e.g.*, US Patent 3,833,686). This process can provide populations of processing aid particles having a mean particle size ranging from 10 to 1,000 nm. It is within the scope of this invention for the populations of processing aid particles to have a mean particle size ranging from 20 to 800 nm; or from 30 to 600 nm; or from 40 to 400 nm.

Presence of At Least Two Different Populations Of Polymeric Particles

Fourthly, the polymeric composition contains at least two different populations of polymeric particles, wherein each has a rubber-containing portion, and wherein the differences are at least one of the following: the void ratio of their rubber containing portions, their chemical compositions, the average sizes of their particles, or the shapes of their particles.

If the difference between the populations is their average particle sizes, there will be a population having a “large” particle size, and a population having a “small” particle size. The average particle size of the large particles is at least 20 percent larger than the average particle size of the small particles. It is within the scope of this embodiment for the average particle size of the large particles to be at least 30 percent larger; or at least 40 percent larger; or at least 50 percent larger than the average particle size of the small particles.

In this embodiment, the large particles typically have a mean particle diameter which ranges from 50 to 7,000 nm. It is within the scope of this invention for the large particles to have a mean particle diameter which ranges from 100 to 5,000 nm; or from 200 to 3,000 nm; or from 300 to 1,000 nm.

On the other hand, the small particles typically has a mean particle diameter which ranges from 10 to 1,000 nm. It is within the scope of this invention for the small particles to

have a mean particle diameter which ranges from 30 to 800 nm; or from 50 to 600 nm; or from 100 to 400 nm.

If the difference between the populations of particles is shape, this can include populations of particles having different morphologies such as: ellipsoidal particles having an aspect ratio greater than 1:1; raspberry-shaped particles; multi-lobe-shaped particles; dumbbell-shaped particles; agglomerated particles; round particles, cylindrical particles, abstract-shaped particles, bi-lobal particles, or circular particles.

If the difference between the populations of particles is the void ratio of their respective rubber-containing portions, the volumetric proportion of the voids defined within one of the populations is at least 20 percent greater than the volumetric proportion of voids defined within the other population of polymeric particles. It is within the scope of this invention for the volumetric proportion of the voids defined within one of the populations is at least 30 percent greater, or at least 40 percent greater, or at least 50 percent greater than the volumetric proportion of voids defined within the other population of polymeric particles.

The above define embodiments of the invention wherein the polymeric composition contains polymeric particles having a rubber-containing portion with an isobutylene polymer component present in an amount of at least 1 weight percent. However, if the polymeric composition contains polymeric particles having a rubber-containing portion with no isobutylene polymer component, or an isobutylene polymer component present in an amount of less than 1 weight percent, then none of the aforementioned four conditions need to be present. It is, however, within the scope of this invention for any one or more of the aforementioned four conditions to, optionally, be present with such a polymeric particle.

The rubber-containing portion of the polymeric particles employed in the practice of the present invention includes at least one of the following blends: (a) an organosiloxane polymer component and an isobutylene polymer component; (b) a vinyl polymer component and an isobutylene polymer component; or (c) an organosiloxane polymer component, a vinyl polymer component and an optional isobutylene polymer component. The individual components of these blends can be present in a single particle, or in different particles, or in a combination thereof.

The proportions of the isobutylene polymer component, the organosiloxane polymer component and the vinyl polymer component in the rubber-containing portion of the

polymeric particles are not particularly limited, and may be suitably adjusted in accordance with the purposes. The isobutylene polymer component, the organosiloxane polymer component and the vinyl polymer component used in making the blends present in the rubber-containing portion of the polymeric particles are now described.

In one embodiment, essentially no isobutylene component is present. In another embodiment, the isobutylene polymer component is present in an amount ranging from 0.01 to 0.9 weight percent; or from 0.01 to 0.7 weight percent; or from 0.01 to 0.5 weight percent. In still another embodiment, the isobutylene polymer component is present in an amount ranging from 1 to 99 weight percent; or from 5 to 95 weight percent; or from 10 to 90 weight percent. These weight percentages are based on the total weight of the polymeric particle's rubber containing portion.

In one embodiment, the organosiloxane polymer component is present in an amount ranging from 1 to 50 weight percent; or from 5 to 40 weight percent; or from 10 to 30 weight percent. In another embodiment, the organosiloxane polymer component is present in an amount ranging from 51 to 95 weight percent; or from 55 to 85 weight percent; or from 65 to 75 weight percent. These weight percentages are based on the total weight of the polymeric particle's rubber containing portion.

In one embodiment, the vinyl polymer component is present in an amount ranging from 1 to 50 weight percent; or from 5 to 45 weight percent; or from 10 to 40 weight percent. In another embodiment, the vinyl polymer component is present in an amount ranging from 51 to 89 weight percent; or from 60 to 85 weight percent; or from 65 to 80 weight percent. In still another embodiment, the vinyl polymer component is present in an amount ranging from 90 to 99 weight percent; or from 92 to 98 weight percent; or from 93 to 97 weight percent. These weight percentages are based on the total weight of the polymeric particle's rubber containing portion.

The isobutylene polymer component which can be employed when practicing certain embodiments of this invention is typically an isobutylene polymer containing at least 50% of units derived from isobutylene. The isobutylene polymer is obtained by a method such as cationic polymerization.

Typically, the isobutylene polymer contains at least one reactive functional group at its molecular end, or in its molecular chain, or in both locations. The units other than the

isobutylene unit, which constitute the isobutylene polymer, include a unit derived from an initiator used when preparing the isobutylene polymer, a unit derived from a cationically polymerizable monomer which is used in the preparation of the isobutylene polymer as occasion demands, a unit having a reactive functional group introduced into the molecular end or the molecular chain (including side chains) of the isobutylene polymer.

Examples of the unit derived from an initiator used when preparing an isobutylene polymer that can be used when practicing this invention are: $--C(CH_3)_2--C_6H_4--C(CH_3)_2--$; $--C(CH_3)_2--C_6H_4--(CH_2)_2--C_6H_4--C(CH_3)_2--$; $--C(CH_3)_2--(CH_2)_2--C(CH_3)_2--$; $C_6H_5--C(CH_3)_2--$. Of these, $--C(CH_3)_2--C_6H_4--C(CH_3)_2--$ is preferable from the viewpoint of introduction rate of functional group to the isobutylene polymer.

Examples of the unit derived from a cationically polymerizable monomer which is used in the preparation of the isobutylene polymer as occasion demands are: a unit derived from isoprene monomer, a unit derived from butadiene monomer, a unit derived from styrene monomer, a unit derived from α -methylstyrene monomer, a unit derived from a vinyl ether monomer, and a unit derived from 1-butene monomer. Among these, the unit derived from isoprene monomer is preferable from the viewpoint of a reactivity with isobutylene.

Examples of the unit derived from a cationically polymerizable monomer which is used in the preparation of the isobutylene polymer as occasion demands are: a unit derived from isoprene monomer, a unit derived from butadiene monomer, a unit derived from styrene monomer, a unit derived from α -methylstyrene monomer, a unit derived from a vinyl ether monomer, and a unit derived from 1-butene monomer. Among these, the unit derived from isoprene monomer is preferable from the viewpoint of a reactivity with isobutylene.

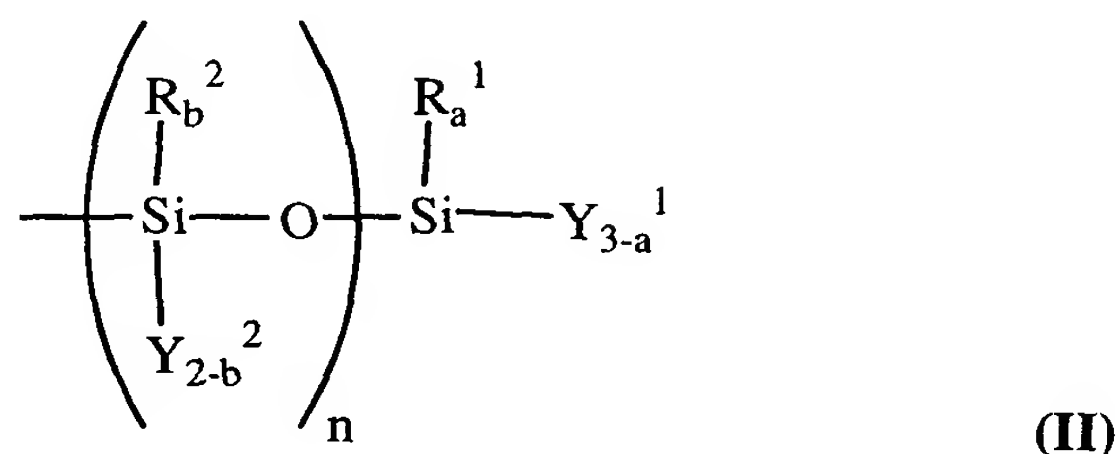
The unit having a reactive functional group introduced into the molecular end or the molecular chain includes a unit having a group as represented by the formula (I) described below, *e.g.*, dimethoxymethylsilyl group, trimethoxysilyl group, diethoxymethylsilyl group, methoxydimethylsilyl group, allyl group, vinyl group, methacryloyl group, acryloyl group or isopropenyl group, a unit having a group containing an unsaturated double bond derived, for instance, from a conjugated diene monomer, a unit derived from isoprene monomer, and a unit derived from butadiene monomer. Among these, the unit derived from isoprene monomer is preferable from the viewpoint of ease in the introduction, and the unit having dimethoxymethylsilyl group is preferable from the viewpoint of the reactivity.

Examples of the unit having a reactive functional group introduced into the molecular end, or the molecular chain of the isobutylene polymer, or both are, for instance, units represented by the formula (I):



(I)

wherein R is a single bond or a divalent hydrocarbon group having 1 to 20 carbon atoms, and X is a halogen atom, *e.g.*, chlorine atom or bromine atom, vinyl group, allyl group, isopropenyl group, acryloyl group, methacryloyl group, epoxy group, amino group, cyano group, isocyano group, cyanate group, isocyanate group, carboxyl group, acid anhydride residue, hydroxyl group, mercapto group or a silicon-containing group represented by the formula (II):



wherein R^1 and R^2 are individually a monovalent hydrocarbon group having 1 to 20 carbon atoms or a triorganosiloxy group, Y^1 and Y^2 are individually hydroxyl group or a hydrolyzable group, *e.g.*, hydrogen atom, alkoxyl group, acyloxy group, ketoximate group, amino group, amido group, aminoxy group, mercapto group or alkenyloxy group, and may be the same or different when they exist two or more, a is 0 or an integer of 1 to 3, b is 0 or an integer of 1 to 2, and n is 0 or an integer of 1 to 18; provided that each of R^1 , R^2 , Y^1 and Y^2 themselves may be the same or different when each group exists plurally.

The halogen atom identified as X in the formula (I) includes, for instance, chlorine atom and bromine atom. Also, the hydrolyzable group identified as Y^1 and Y^2 in the formula (II) includes, for instance, hydrogen atom, alkoxyl group, acyloxy group, ketoximate group, amino group, amido group, aminoxy group, mercapto group or alkenyloxy group. Of these, an alkoxyl group is particularly preferable from the viewpoints of mild hydrolyzability and ease in handling.

Isobutylene polymers that can be used when practicing this invention can have in the molecular end, or in the molecular chain, or in both locations, at least one of the following reactive functional groups: a halogen-containing group, a radically reactive unsaturated group such as vinyl group, allyl group, isopropenyl group, acryloyl group or methacryloyl group, and a silicon-containing group. These are preferable from the viewpoints of availability and ease in handling. Also, isobutylene polymers having a reactive functional

group derived from a conjugated diene monomer in the molecular end or the molecular chain are preferable from the viewpoints of versatility and low cost. Isobutylene polymers having allyl group or a silicon-containing group as a reactive functional group are preferable from the viewpoints of conversion and enhancement of impact resistance. Among the above-mentioned isobutylene polymers, an allyl group-terminated polyisobutylene which has allyl group as a reactive functional group at the molecular end and a silicon-containing group-terminated polyisobutylene which has a silicon-containing group as a reactive functional group at the molecular end are particularly preferred from the viewpoint of ease in controlling the crosslinking structure.

The number average molecular weight of the isobutylene polymers that can be used when practicing this invention is typically from 300 to 1,000,000 g/mol; or from 500 to 500,000 g/mol. If the number average molecular weight is less than 300 g/mol, too much unreacted material remains, and if the number average molecular weight is more than 1,000,000 g/mol, the viscosity is high and it tends to be difficult to handle.

Examples of the isobutylene polymer having a reactive functional group represented by the formula (I) at the molecular end are, for instance, a low molecular weight polyisobutylene oil having an average molecular weight of about 300 to about 5,000 g/mol, *e.g.*, Nisseki Polybutene HV-3000 (isopropenyl group-terminated isobutylene polymer, made by Nippon Sekiyu Kagaku Kabushiki Kaisha), Nissan Polybutene 200N (isopropenyl group-terminated isobutylene polymer, made by NOF Corporation) and Idemitsu Polybutene 300R (isopropenyl group-terminated isobutylene polymer, made by Idemitsu Sekiyu Kagaku Kabushiki Kaisha); a high molecular weight polyisobutylene having a viscosity average molecular weight of 30,000 to 60,000 g/mol and commercially available under the trade mark "Tetolax" (isopropenyl group-terminated isobutylene polymer, made by Nippon Petrochemicals Co., Ltd.); a polyisobutylene having an allyl terminal group as disclosed in JP-B-7-53768; and a polyisobutylene having a silicon-containing terminal group as disclosed in JP-B-4-69659.

The reactive functional group which can be present in the molecular chain of the isobutylene polymer includes, for instance, a group having an unsaturated double bond derived from a diene monomer. Typical example of such a diene monomer is, for instance, isoprene.

Examples of the isobutylene polymer having a group containing the above-mentioned radically reactive unsaturated group in the molecular chain are a copolymer comprising units derived from isobutylene monomer and units derived from isoprene monomer, which is generally known as so-called "butyl rubber" and is commercially available, *e.g.*, JSR Butyl 268 (isobutylene-isoprene copolymer, made by Japan Synthetic Rubber Co., Ltd.), KALAR5263 and KALENE800 (isobutylene-conjugated diene copolymer, both available from HARDMAN INCORPORATED).

As the isobutylene polymers used in the present invention, those having in the molecular end, or in the molecular chain, or in both locations, at least one reactive functional group selected from a halogen-containing group, vinyl group, allyl group, isopropenyl group, acryloyl group, methacryloyl group and a silicon-containing group are preferable from the viewpoints of availability and ease in handling. Also, isobutylene polymers having a reactive functional group derived from a diene monomer in the molecular end, or in the molecular chain, or in both locations, are preferable from the viewpoints of versatility and low cost. Isobutylene polymers having allyl group or a silicon-containing group as a reactive functional group are also preferable from the viewpoints of enhancement of impact resistance and transparency. Further, among these isobutylene polymers, an allyl group-terminated polyisobutylene which has allyl group as a reactive functional group at the molecular end and a silicon-containing group-terminated polyisobutylene which has a silicon-containing group as a reactive functional group at the molecular end are particularly preferred from the viewpoint of ease in controlling the crosslinking structure.

The isobutylene polymers used in certain embodiments of the present invention may contain a moiety derived from a crosslinking agent or a graftlinking agent in order to raise the gel fraction. Preferably, the content of the moiety derived from a crosslinking agent or a graftlinking agent is from 0 to 20%, especially from 0 to 10%, with respect to the moiety derived from a crosslinking agent, and is from 0 to 20%, especially from 0 to 10%, with respect to a graftlinking agent. These ranges are desirable from the viewpoint of a balance between impact resistance-improving effect and processability.

The organosiloxane polymer component used when practicing certain embodiments of this invention includes an organosiloxane polymer. Such a polymer can be obtained by a ring-opening polymerization or condensation polymerization of an organosiloxane monomer. Examples of such include: hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane,

decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, trimethyltriphenylcyclotrisiloxane, tetramethyltetraphenylcyclotetrasiloxane, octaphenylcyclotetrasiloxane, octaethylcyclotetrasiloxane, dimethyldimethoxysiloxane, diethyldimethoxysilane, diethyldiethoxysilane, diphenyldimethoxysilane, and the like. These may be used alone or in admixture thereof.

The organosiloxane polymer may contain a moiety derived from a crosslinking agent or a graftlinking agent. The content of the moiety derived from a crosslinking agent is from 0 to 20%, especially from 0 to 10%. The content of the moiety derived from a graftlinking agent is from 0 to 20%, especially from 0 to 10%. These ranges are desirable from the viewpoint of a balance between impact resistance-improving effect and processability.

The vinyl polymer component used when practicing certain embodiments of this invention includes a vinyl polymer. Such a polymer can be derived from radical polymerization of a vinyl monomer.

Any radically polymerizable unsaturated compounds can be used as the vinyl monomer without any restriction. Examples of such vinyl monomers include: an acrylic ester such as methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate or n-octyl acrylate; a methacrylic ester such as methyl methacrylate, ethyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate or isobornyl methacrylate; an aromatic alkenyl compound such as styrene, α -methylstyrene, p-methylstyrene or vinyltoluene; a vinyl cyanide compound such as acrylonitrile or methacrylonitrile; a conjugated diene compound such as butadiene or isoprene; a halogen-containing unsaturated compound such as vinyl chloride or vinylidene chloride; and other vinyl compounds. These may be used alone or in admixture thereof. Of these, n-butyl acrylate, methyl methacrylate and styrene are preferable from the viewpoints of versatility, low cost and ease in handling.

The vinyl polymer may contain a moiety derived from a crosslinking agent or a graftlinking agent. The content of the moiety derived from a crosslinking agent is from 0 to 20%, especially from 0 to 10%. The content of the moiety derived from a graftlinking agent is from 0 to 20%, especially from 0 to 10%. These ranges are desirable from the viewpoint of a balance between impact resistance-improving effect and processability.

The above-mentioned isobutylene polymer component, organosiloxane polymer component and vinyl polymer component of the rubber-contain portion of the polymeric particles of the present invention may be, as stated above, components derived from polymers containing a moiety derived from a crosslinking agent or a graftlinking agent.

If used, the crosslinking agent is typically a compound having a plurality of functional groups in a molecule, and these plural functional groups have the same reactivity. The graftlinking agent is typically a compound having a plurality of functional groups in a molecule, and these plural functional groups have a different reactivity. The crosslinking agent is used for the purpose of producing crosslinkages in a single polymer component, and the graftlinking agent is used for the purpose of producing crosslinkages between different polymer components. In practical action, however, there are cases where the crosslinking agent may produce crosslinkages between different polymer components, and the graftlinking agent may produce crosslinkages in a single polymer component, so the distinction of the actions of both agents is not definite.

Examples of the crosslinking agents that can be used when practicing certain embodiments of this invention include: a trifunctional silane compound such as trimethoxymethylsilane or triethoxyphenylsilane; a tetrafunctional silane compound such as tetramethoxysilane, tetraethoxysilane, tetrapropoxysilane or tetrabutoxysilane; a difunctional vinyl compound such as ethylene glycol dimethacrylate, propylene glycol dimethacrylate, 1,3-butylene glycol dimethacrylate, 1,4-butylene glycol dimethacrylate or divinyl benzene; and a trifunctional vinyl compound such as triallyl cyanurate or triallyl isocyanurate. These may be used alone or in admixture thereof. These crosslinking agents can be suitably selected according to the presence or absence and the kind of a functional group in the isobutylene polymer, and the kind of a polymer to be crosslinked.

Examples of the graftlinking agents that can be used when practicing certain embodiments of this invention include: a (meth)acrylic functional silane compound such as β -methacryloyloxyethyltrimethoxymethylsilane,
 γ -methacryloyloxypropylmethoxydimethylsilane,
 γ -methacryloyloxypropyltrimethoxymethylsilane,
 γ -methacryloyloxypropyltrimethoxysilane,

γ - methacryloyloxypropylethoxydiethylsilane,

γ - methacryloyloxypropyldiethoxymethylsilane,

γ - methacryloyloxypropyltriethoxysilane,

δ - methacryloyloxybutyldiethoxymethylsilane,

γ - acryloyloxypropyldimethoxymethylsilane or

γ - acryloyloxypropyltrimethoxysilane; an ethylenic functional silane compound such as vinyltrimethoxysilane, vinyl dimethoxymethylsilane, vinyltriethoxysilane,

p-vinylphenyltrimethoxysilane or

p- vinylphenyldimethoxymethylsilane; a mercapto functional silane compound such as

γ -mercaptopropyltrimethoxysilane or

γ - mercaptopropyldimethoxymethylsilane; and a vinyl compound such as allyl methacrylate.

These may be used alone or in admixture thereof. These graftlinking agents can be suitably selected according to the presence or absence and the kind of a functional group in the isobutylene polymer, and the kind of a polymer to be graftlinked.

The crosslinking agent and the graftlinking agent may be used alone or in admixture of two or more of them. The amount of the crosslinking agent or the graftlinking agent is preferably at least 0.1 part (part by weight, hereinafter the same), more preferably at least 0.3 part, per 100 parts of the total of the isobutylene polymer which constitutes the isobutylene polymer component, the organosiloxane monomer which constitutes the organosiloxane polymer component, and the vinyl monomer which constitutes the vinyl polymer component, so that the effect of use of these agents is sufficiently exhibited. It is also preferable that the amount of the crosslinking agent and/or the graftlinking agent is at most 25 parts, especially at most 10 parts, per 100 parts of the total of the isobutylene polymer, the organosiloxane monomer and the vinyl monomer, so that the obtained crosslinked rubber particles exhibit a sufficient impact resistance-improving effect and rise of cost is suppressed.

The process for preparing crosslinked rubber-containing polymeric particles used when practicing this invention is not limited. It is possible to prepare the particles in a single stage or multistage by utilizing emulsion polymerization method or micro- suspension

polymerization method. For example, a latex containing crosslinked rubber particles can be made by mixing, with shearing, a liquid mixture of an isobutylene polymer, an organosiloxane monomer, a vinyl monomer, a crosslinking agent, a graftlinking agent and optionally a usual radical polymerization initiator with water in the presence of an emulsifier and, optionally, a dispersion stabilizer such as a higher alcohol; and, using a homogenizer to emulsify the mixture and carry out the polymerization. At that time, a polymerization reaction of the organosiloxane monomer can be accelerated by acidifying the reaction system with an inorganic acid such as hydrochloric acid, sulfuric acid or nitric acid, or an organic acid having a surface activity such as alkylbenzene sulfonate, alkyl sulfonate or alkyl sulfate.

As mentioned above, the rubber-containing polymeric particles of the present invention may contain a plurality of polymer components in a single particle, or may be composed of particles each comprising a single polymer component. The particles containing a plurality of polymer components in a single particle can be prepared by a method wherein respective components are previously mixed uniformly, emulsified and subjected to a reaction, a method wherein, in the presence of seed particles composed of a single polymer component, other components are further subjected to polymerization (seed polymerization), a method wherein particles each comprising a single polymer component are mixed and are then agglomerated to enhance the particle size by adding an acid such as hydrochloric acid or a salt such as sodium sulfate, or other methods. At that time, the state inside the obtained particles can be controlled by the preparation method, the proportions of respective components, or the order of reaction.

The thus prepared latex containing rubber particles can be directly used or can also be used after separating and recovering the rubber-containing polymeric particles.

The polymeric particles of the present invention can also be made by subjecting the above-mentioned rubber-containing particles to a graft copolymerization with a vinyl monomer. This typically forms a particle having a core/shell configuration.

The vinyl monomer to be graft-copolymerized onto the rubber-containing particles includes various kinds of vinyl monomers, for instance, an acrylic ester such as methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate or n-octyl acrylate; a methacrylic ester such as methyl methacrylate, ethyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate or isobornyl methacrylate; an aromatic alkenyl compound such as styrene, α -methylstyrene or p-

methystyrene; a vinyl cyanide compound such as acrylonitrile or methacrylonitrile; a conjugated diene compound such as butadiene or isoprene; and a halogen-containing unsaturated compound such as vinyl chloride or vinylidene chloride. These may be used alone or in admixture thereof. These vinyl monomers are suitably selected in accordance with a combination with various resins to be improved in impact resistance.

Also, in the graft polymerization, either or both of the crosslinking agent and the graftlinking agent can be used, as occasion demands. The total amount of the crosslinking agent and the graftlinking agent is from 0 to 20 parts, especially 0 to 10 parts, per 100 parts of the vinyl monomer used in the graft polymerization.

The proportions of the rubber-containing portion and the vinyl monomer portion is not limited. Typically, based on the whole weight of the polymeric particles, in one particular embodiment, the proportion of the rubber-containing portion is from 30 to 89%, or from 40 to 85%, or from 50 to 80%. In another particular embodiment, the proportion of the rubber-containing portion is from 90 to 100%, or from 92 to 99%, or from 93 to 98%.

On the other hand, in one particular embodiment, the proportion of the vinyl monomer portion is from 11 to 70%, or from 15 to 60%; or from 20 to 50%. In another particular embodiment, the proportion of the vinyl monomer portion is from 0 to 10%, or from 1 to 8%; or from 2 to 7%.

The graft efficiency in the crosslinked rubber-containing polymeric particles of the present invention is not limited. In certain circumstances, it is preferred if the graft efficiency is at least 30%, or at least 50%.

The process for preparing the rubber-containing polymeric particles of the present invention is not particularly limited. However, when the polymeric particles further include a vinyl monomer portion, the polymeric particles can be prepared, for example, by a process wherein the above-mentioned vinyl monomer is added to the above-mentioned rubber-containing particle latex and polymerized by a radical polymerization technique in a single stage or multi-stages to give a latex of the graft copolymer. In case that the rubber-containing particle latex has been prepared in a reaction system made acidic, the rubber-containing particle latex may be neutralized prior to conducting the graft polymerization by adding an aqueous solution of an alkali such as sodium hydroxide, potassium hydroxide or sodium carbonate to the latex.

In some instances, the novel polymeric composition of the present invention has an intermediate layer interposed between the rubber-containing core portion and the vinyl monomer shell portion (hereinafter referred to as the "intermediate shell"). If present, the intermediate shell typically comprises units derived from methyl methacrylate. Generally, at least 50 weight percent of the intermediate shell is comprised of methyl methacrylate. It is within the scope of this embodiment of the invention for an intermediate shell to be comprised essentially of methyl methacrylate. Thus, the intermediate shell may be a homopolymer of methyl methacrylate, a copolymer of methyl methacrylate with a small amount, such as from about 1 to about 20 parts of an alkyl acrylate or an alkyl methacrylate, such as ethyl methacrylate or butyl acrylate, a copolymer of methyl methacrylate with styrene, and a copolymer of methyl methacrylate with methacrylic acid.

When present, the intermediate shell is typically at least 2 weight percent of the polymeric particles making up the novel polymeric composition. It is within the scope of this embodiment for the intermediate shell to be at least 5 weight percent of the polymeric particle, or at least 7 weight percent of the polymeric particle. On the other hand, when present, the intermediate shell is typically at most 25 weight percent of the polymeric particle. It is within the scope of this embodiment of the invention for the intermediate shell to be at most 20 weight percent of the polymeric particle, or at most 15 weight percent of the polymeric particle. The preferred weight percentage depends upon the desired end use.

The intermediate shell polymer may be partially or totally attached to or grafted to the rubber-containing portion of the polymeric particle. It may further contain from about 0.05 weight percent to about 5 weight percent of one or more multi-unsaturated monomers, as defined above.

The ratio of core to intermediate shell is as defined to ensure that the highest impact efficiency can be achieved whilst leaving a shell to act as a compatibilizing layer between the rubbery polymer and the matrix resin. The use of a low level of intermediate shell means that the intermediate polymeric particle will not have a particle size much larger than the original core particle.

In this specific embodiment, the reaction conditions for formation of both the intermediate and final shells are those under which essentially no new polymer particles are formed. These conditions are well known, and generally relate to avoiding formation of new polymer particles in separate soap-stabilized micelles. Normally, little or no new emulsifier

is added, and the soap concentration is maintained below the critical micelle concentration, which is known or can be determined for most emulsifiers. Further, the use of highly water-soluble monomers is avoided, to avoid formation of separate particles. However, if the polymer is water insoluble, then water soluble monomers can be used.

It is impossible to define the specific conditions for each emulsion polymerization since every process is different. However, a common rule that can be used when determining the ideal conditions is to test the further polymerization on a small scale by adding no additional emulsifier to a system already low in emulsifier; if the emulsion remains stable, then a larger reaction may be conducted.

Another embodiment of this invention relates to novel plastic resin compositions which contain a plastic resin component and any of the novel polymeric compositions disclosed herein. Examples of the plastic resins to which the novel polymeric compositions of the present invention are applicable include: polymethyl methacrylate resin, polyvinyl chloride resin, polyvinylidene chloride resin, polyethylene resin, polypropylene resin, cyclic olefin copolymer resin, polycarbonate resin, polyester resin, a mixture of polycarbonate resin and polyester resin, a homopolymer or copolymer of 70 to 100% of at least one vinyl monomer selected from the group consisting of an aromatic alkenyl compound, a vinyl cyanide compound and a (meth)acrylic acid ester and 30 to 0% of at least one other monomer copolymerizable therewith, *e.g.*, other vinyl monomer such as ethylene, propylene or vinyl acetate and a conjugated diene monomer such as butadiene or isoprene, polystyrene resin, polyphenylene ether resin, a mixture of polystyrene resin and polyphenylene ether resin, and the like. A wide range of plastic resins are usable without being limited to the exemplified resins. Polymethyl methacrylate resin, polyvinyl chloride resin, polypropylene, cyclic olefin copolymers, polycarbonate resin and polyester resin are particularly preferable since effects of improvement in weatherability, impact resistance and the like are easy to be produced.

In one specific embodiment, the amount of the novel polymeric compositions added to a plastic resin is typically from 50 to 95 parts, and more typically from 60 to 90 parts, per 100 parts of the thermoplastic resin. In this embodiment, the resulting product can be used as a concentrate which is, thereafter, added to a plastic resin producing process to produce a final product.

In another specific embodiment, the amount of the novel polymeric compositions added to a plastic resin is typically from 0.1 to 45 parts, and more typically from 1 to 40

parts, per 100 parts of the plastic resin. In this embodiment, the resulting product is the final product. If the amount of the novel is less than 0.1 part, the impact resistance-improving effect tends to become insufficient, and if the amount is more than 50 parts, the properties of the plastic resin tend to be impaired.

The resulting plastic resin composition may further contain one or more of the following: lubricant, processing aid, rheology modifier, dye, pigment, flame retardant, thermal stabilizer, antioxidant, antiozonant, ultraviolet stabilizer, mold release agent, reinforcing filler or non-reinforcing filler. If present, the reinforcing filler may be least one of the following: glass fibers, glass spheres, talc, or mica. In the case of a polyvinyl chloride resin composition made in accordance with this embodiment of the invention, the novel resin composition may also contain a heat distortion improver, such as a polyglutarimide.